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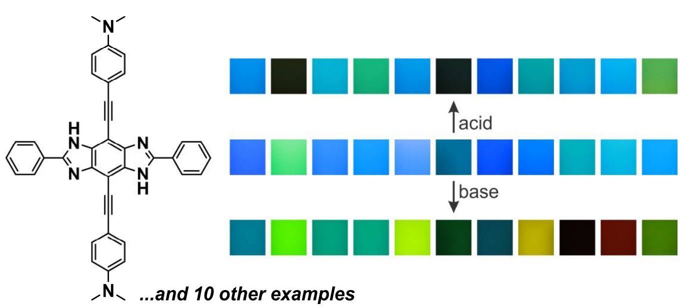


Abstract

A series of eleven cross-conjugated cruciform fluorophores based on a benzobisimidazole nucleus has been synthesized and characterized. Like in their previously reported benzobisoxazole counterparts, the HOMOs of these new fluorophores are localized along the vertical bisethynylbenzene axes, while their LUMOs remain relatively delocalized across the molecule—except in cruciforms substituted with electron-withdrawing groups along the vertical axis. Benzobisimidazole cruciforms exhibit pronounced response to deprotonation in their UV/Vis absorption and emission spectra, but their re-sponse to protonation is significantly attenuated.

INTRODUCTION

Cross-conjugated molecular cruciforms[1] have been a subject of much scrutiny in recent years as their modular optoelectronic properties make them versatile elements in sensing and molecular electronics applications. Nuckolls,[2] Jeffries-EL,[3] and we[4] have extensively studied molecular cruciforms based on the central benzobisoxazole motif, represented by structure **1** (Figure 1). Our group has demonstrated that benzobisoxazole cruciforms represent a viable fluorescent sensor for a broad variety of analytes, and that they are capable of detecting minute structural differences between those analytes.[3d,3f] In a related effort, we have shown that cruciforms can be "cut in half" and that the oxazole nucleus can be replaced by an imidazole, to give L-shaped half-cruciforms of the general structure **2**.[5] Bielawski et al. have studied fluorophores based on benzobisimidazolium salts represented by general structure **3**.[6]

In this contribution, we present "the missing link" in this series of fluorophores: the X-shaped benzobisimidazole-based cruciforms **4a**–**l** (Scheme 1). These new fluorophores are direct analogs of **1** in which the two oxazole nuclei have been replaced with imidazoles.

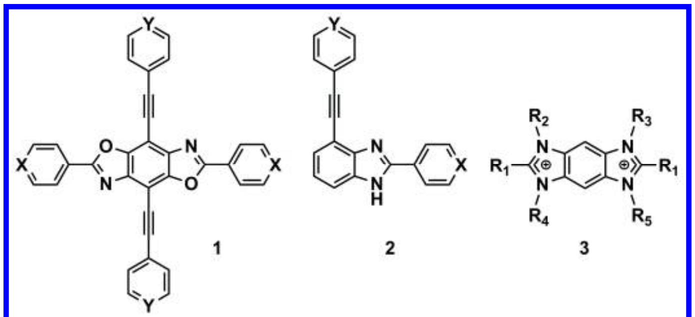
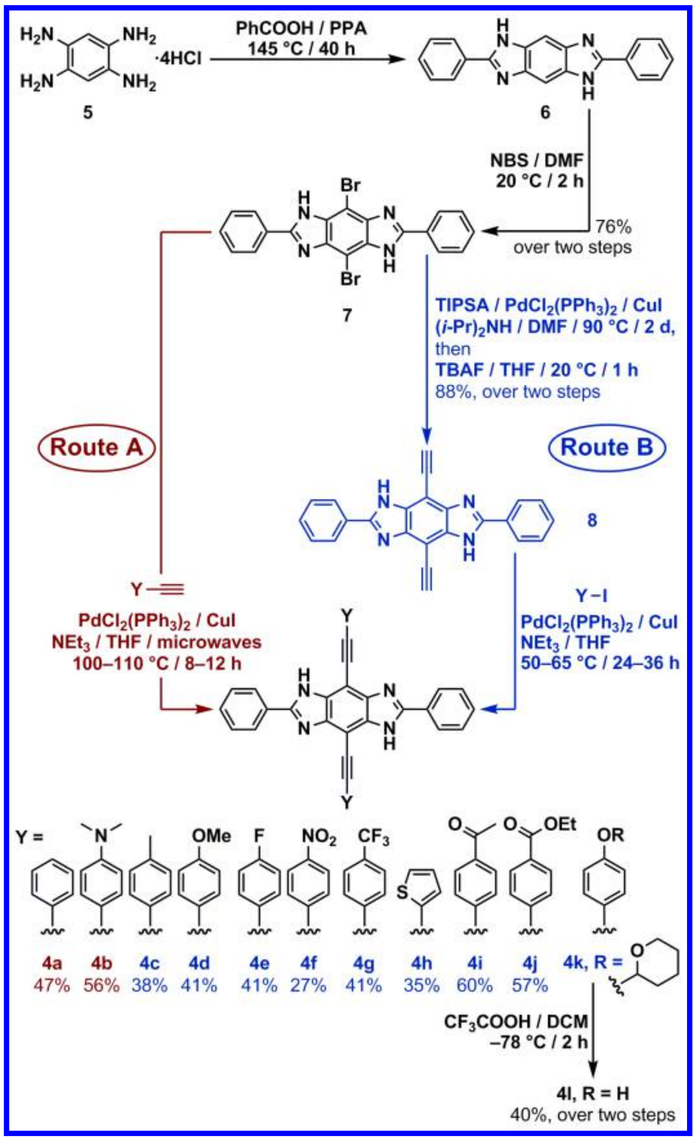


Figure 1. Previous examples of fluorophores based on cross-conjugated benzobisoxazole (**1**) and benzimidazole (**2**) geometries, and benzobisimidazole motif (**3**).

RESULTS AND DISCUSSION

Synthesis. Despite structural similarity between **1** and **4**, their syntheses had to be approached quite differently. Cruciforms **1** could be easily elaborated from the readily available 2,5-diamino-3,6-dibromobenzene-1,4-diol,[7] whose *o*-aminophenol functionalities engaged in acyl condensation to generate the horizontal axis, while the two bromine substituents reacted in a Sonogashira coupling to establish the vertical axis. As the corresponding 1,2,4,5-tetraamino-3,6-dibromobenzene[8] proved difficult to prepare and handle, we chose to begin the synthesis of benzobisimidazole cruciforms with a hydrochloride salt of 1,2,4,5-tetraaminobenzene (**5**, Scheme 1).[9] Its condensation with benzoic acid in the presence of polyphosphoric acid (PPA) yielded intermediate **6**,[3g] which was then doubly brominated on the central benzene ring with *N*-bromosuccinimide (NBS) to produce compound **7**. The vertical axis was established by the subsequent Sonogashira coupling with a terminal alkyne bearing functionalities of interest, yielding cruciforms **4a** and **4b** (route A, highlighted in dark red in Scheme 1). In an alternative approach (route B, highlighted in blue), the roles of coupling partners were switched: compound **7** was first reacted with tris(isopropylsilyl)acetylene (TIPSA) and then desilylated to reveal two terminal alkyne functionalities in precursor **8**. Compound **8** was subsequently functionalized through a second Sonogashira coupling to produce cruciforms **4c**–**k**. Cruciform **4l** was obtained after acidic hydrolysis of the tetrahydropyranyl (THP) protecting group in **4k**.

It should be noted that this synthetic route was plagued with difficulties. First, compound **5** is very difficult to handle on account of its sensitivity to oxidation and high polarity. Second, analogs of the highly insoluble intermediate **6** bearing other functional groups along the horizontal axis proved difficult to prepare and impossible to purify, and their subsequent bromination yielded mixtures of products. Thus, we were not able to effectively vary the substitution along the horizontal axis of these cruciforms. Finally, the closing Sonogashira couplings proceeded in moderate yields (27–60%), which was likely a consequence of the low solubility of the precursors.



Scheme 1. Synthesis of Benzobisimidazole Cruciforms **4a**–**l**.

Computational Studies. Frontier molecular orbitals (FMOs) of cruciform **4a**–**4j** and **4l** have been calculated using Gaussian 09W[10] software using the B3LYP hybrid density functional and 3-21G as the basis set. FMOs of two exemplary cruciforms **4a** and **4f** are shown in Figure 2. In both systems, the highest occupied molecular orbital (HOMO) resides dominantly along the vertical axis. As observed previously for the related benzobisoxazole-based cruciforms,[3g] this vertical localization of the HOMOs is a consequence of orbital properties of the benzobisimidazole core and is largely independent of the substitution. The lowest unoccupied molecular orbital (LUMO) of **4a** is in contrast delocalized across the molecule. In the case of a cruciform substituted with electron-withdrawing groups along the vertical axis—such as **4f** (Figure 2, bottom)—the LUMO also resides along the electron-poor vertical axis of the molecule. As synthetic access to cruciform variants with a different substitution on the horizontal axis was restricted, we were unable to probe the effects of placing strongly electron-withdrawing or electron-donating groups along the horizontal axis.

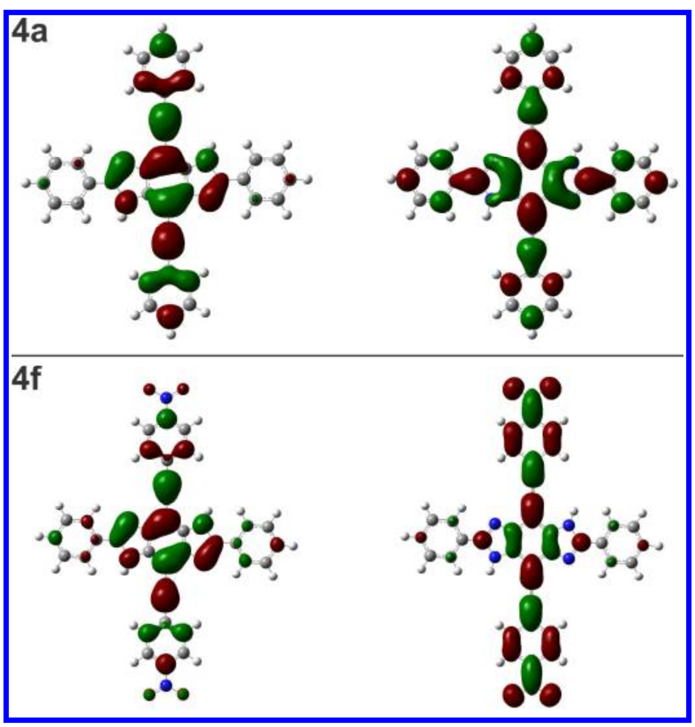


Figure 2. HOMOs (left) and LUMOs (right) of cruciforms **4a** and **4f** (calculated in Gaussian, using B3LYP hybrid density functional and 3-21G basis set).

Optical Properties. Compounds **4a**–**l** are yellow to red powders with moderate solubility in most common organic solvents. Their ^{1}H NMR spectra are complicated by facile tautomerization of both imidazoles, but are otherwise consistent with their structures. They are highly fluorescent[11] in solution and mildly in the solid state when irradiated with a handheld UV lamp (λ_{exc}=365 nm). UV/Vis absorption and fluorescence emission spectra of **4a**–**j** and **4l** are shown in Figure 3 and summarized in Table 1. UV/Vis absorption spectra (Figure 3, top) of all cruciforms are essentially superimposable with a single broad absorption band centered between 380 and 395 nm. The only exception is **4b**, whose absorption spectrum shows an additional band at 425 nm. In their fluorescence emission spectra (Figure 3, bottom), a somewhat greater level of distinction can be achieved. Compound **4b** is a clear outlier, with a relatively featureless emission band at 486 nm. All other cruciforms' emission spectra show two distinct maxima: a more intense one, centered between 426 (for **4e**) and 456 (for **4i**) nm, and a lower-intensity band, centered between 452 (for **4e**) and 483 (for **4i**) nm. Most of these trends are visible by the naked eye (see Figure 5 below), in that colors of all cruciforms except **4b** look similar under both UV and visible light.

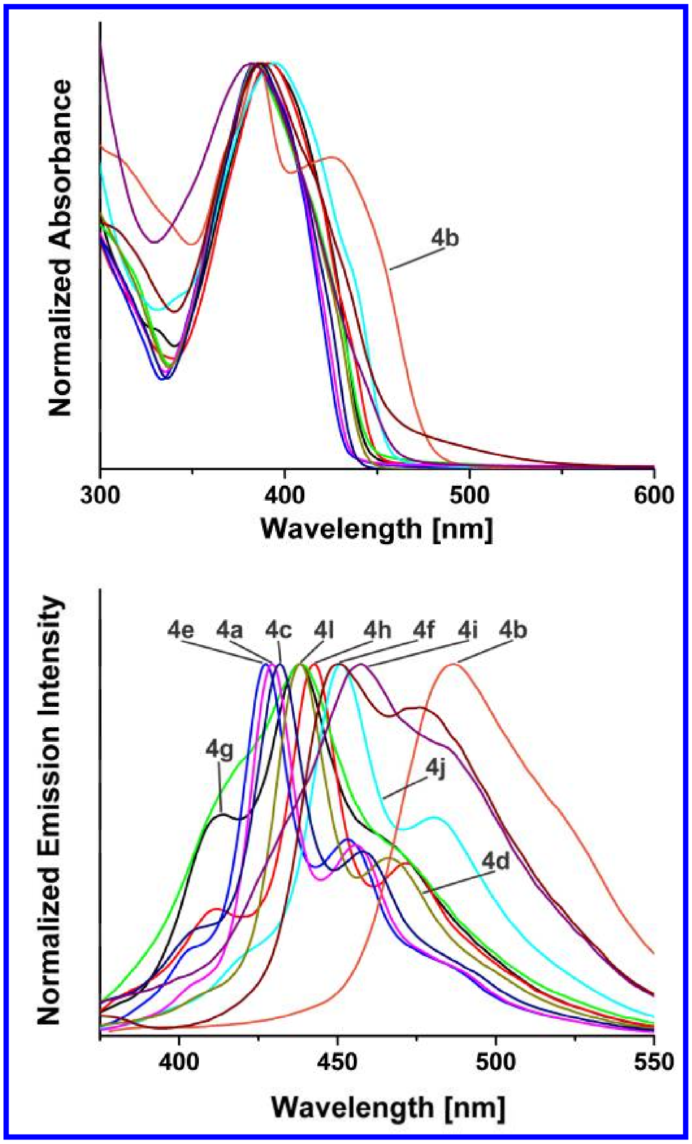


Figure 3. Normalized UV/Vis absorption (top) and emission (bottom) spectra of cruciforms **4a**–**4j** and **4l** in THF. Excitation wavelengths for emission spectra: 335 (**4a**), 348 (**4b**), 336 (**4c**), 337 (**4d**), 333 (**4e**), 339 (**4f**–**4h**), 330 (**4i**–**4j**), 337 (**4l**) nm.

Table 1. Optical Properties and Calculated HOMO–LUMO Gaps for Cruciforms **4a**–**4l**.

Compound	Absorption λ_{max} [nm]	Emission λ_{max} [nm]	Stokes shift [cm^{-1}]	Calculated HOMO–LUMO gap [eV, nm]
4a	386	430	2651	3.02, 411
4b	386	487	5373	3.00, 414
4c	386	432	2759	2.99, 415

4d	385	438	3143	2.91, 426
4e	383	428	2745	3.01, 412
4f	388	451	3600	2.61, 475
4g	392	438	2679	2.99, 415
4h	391	443	3002	2.83, 438
4i	382	458	4344	2.86, 434
4j	395	451	3144	2.90, 428
4l	383	439	3330	2.93, 423

Optical Response to Acids and Bases. In contrast to benzobisoxazole-based cruciforms, these new benzobisimidazole-based systems are amphoteric and were expected to show significant changes in their UV/Vis absorptions and emissions upon both protonation and deprotonation. To experimentally confirm this hypothesis, we performed titrations of **4a**–**l** with both an acid (trifluoroacetic acid, TFA) and a base (tetrabutylammonium hydroxide, TBAOH) in THF. Full experimental details of these titrations are given in the Supporting Information. In general, benzobisimidazole cruciforms show a rather moderate response to acids: with excess acid (−log[TFA]<1.0), a blue shift in absorption of up to $\Delta\lambda = -18$ nm was observed. This set of observation could be rationalized by protonation of benzobisimidazole nitrogen atoms (pK_a = 5.55 for benzimidazolium cation)[12] at high acid concentration. The only cruciform with a different response was **4b** (Figure 4, top), whose significantly more basic $-NMe_2$ groups became protonated at lower concentrations of TFA. In the emission spectra of **4a**–**4j** and **4l**, small but less consistent changes were observed: for some cruciforms, emission shifted minimally toward the red region, while for others it shifted toward the blue or was quenched.

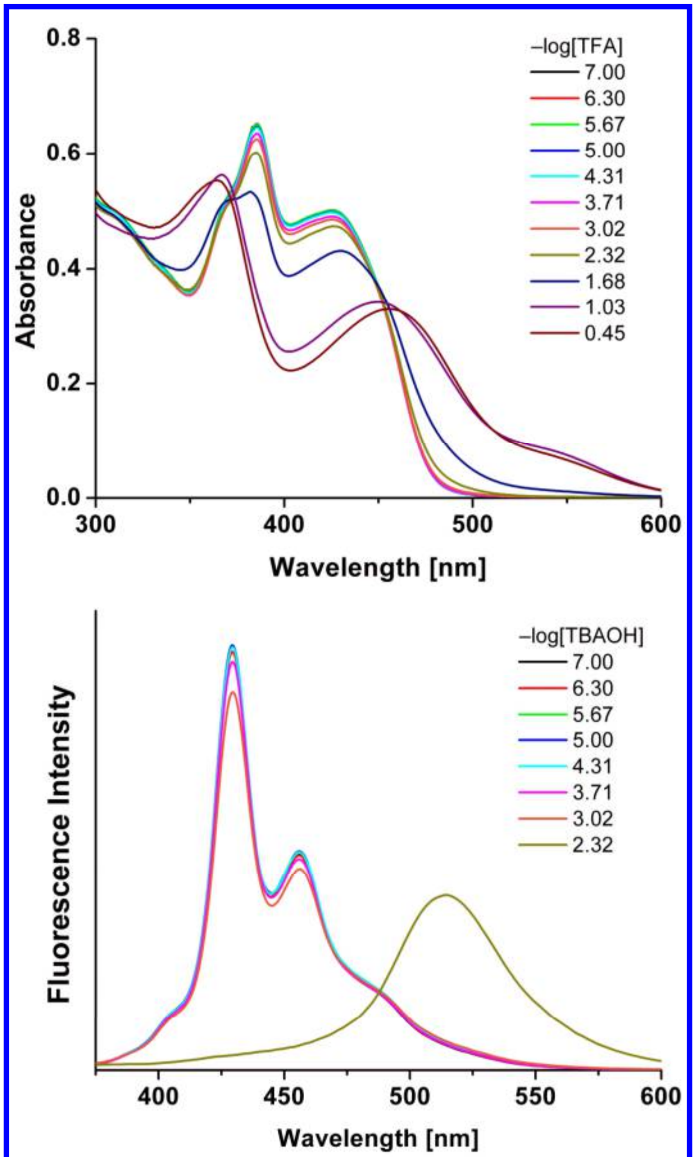


Figure 4. Exemplary titrations of benzobisimidazole cruciforms with acid (top) and base (bottom). On the top, changes in UV/Vis absorption spectra of cruciform **4b** as a function of added TFA. On the bottom, fluorescence response of cruciform **4a** to the addition of TBAOH (λ_{exc}=335 nm). Both titrations were performed in THF.

Response of benzobisimidazole cruciforms to bases is much more dramatic. Upon exposure to high concentrations of base (−log[TBAOH]<2.5), red shifts in absorption of approx. $\Delta\lambda$=+100 nm occurred for all studied cruciforms, and were accompanied by equally significant shifts in the emission (as illustrated for **4a** in Figure 4, bottom); for more acidic **4f**, even lower concentrations of base induced similar shifts. As noticed previously in L-shaped half-cruciforms,[5] deprotonation of benzobisimidazole's N–H moieties (pK_a = 12.78)[12] causes these dramatic changes in fluorescence.

Most of these changes were detectable by the naked eye as well. Digital photographs of vials containing 10^{-5} M solutions of **4a**–**4j** and **4l** under visible and UV light are shown in Figure 5, and the dramatic response of these cruciforms to a base is apparent.

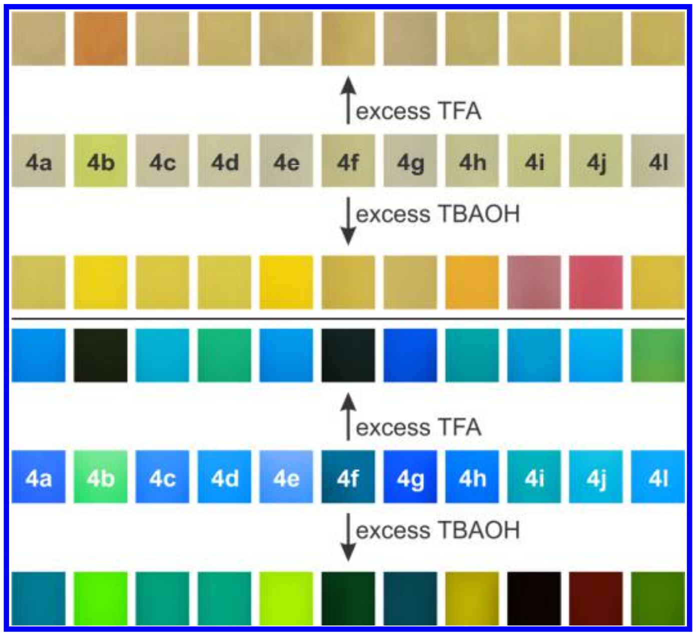


Figure 5. Acid- and base-induced changes in the colors of 10^{-5} M solutions of cruciforms **4a**–**j** and **4l** in THF, as observed under visible (top) and UV (bottom) light. For emission color photographs, λ_{exc}=365 nm, shutter speed 0.05 s.

CONCLUSION

In summary, we have synthesized a series of eleven cross-conjugated cruciform fluorophores based on the benzobisimidazole nucleus, using a combination of acid-catalyzed condensation and Sonogashira coupling. These materials are fluorescent in the solid state and strongly so in dilute solutions. All of them also show a pronounced red shift upon deprotonation of their imidazole N–H functionalities, while, in contrast, their response to acids is much more attenuated. This lack of response is partially a consequence of our inability to synthetically access diverse substitution patterns on the horizontal axis, which in turn, meant that we could modulate the LUMO orbitals of **4a**–**l** only to a limited extent. Thus, unlike in the benzobisoxazole series,[4g] systems with completely spatially separated FMOs could not be produced and studied. At the same time, it is highly encouraging that almost all of the benzobisimidazole cruciforms maintain a certain level of fluorescence regardless of their protonation state. This feature could be explored in the preparation of e.g. fluorescent and guest-responsive porous materials, such as zeolitic imidazolate frameworks (ZIFs),[13] utilizing these cross-conjugated benzobisimidazoles.

EXPERIMENTAL SECTION

General Experimental Methods. All reactions were performed under nitrogen atmosphere in oven-dried glassware. Reagents were purchased from commercial suppliers and used without further purification. Solvents were used as received, except THF and *N,N*-dimethylformamide (DMF), which were degassed by a 30 minute nitrogen purge prior to use in Sonogashira couplings. Compounds 1,5-dichloro-2,4-dinitrobenzene[14] and 1,3-diamino-4,6-dinitrobenzene[15] were synthesized according to literature procedures. Triethylamine (Et_3N) was degassed by a 30 minute nitrogen purge prior to use. Microwave-assisted reactions were performed in a Biotage Initiator 2.0 microwave reactor, producing monochomatic microwave radiation with the frequency of 2.45 GHz. NMR spectra were obtained on spectrometers with working frequencies (for ^{1}H nuclei) of 400, 500, and 600 MHz. All ^{13}C NMR spectra were recorded with simultaneous decoupling of ^{1}H nuclei. ^{1}H NMR chemical shifts are reported in ppm units relative to the residual signal of the solvent ($CDCl_3$: 7.25 ppm, $(CD_3)_2SO$: 2.48 ppm, D_2O: 4.79 ppm, $(CD_3)_2CO$: 2. 05 ppm). All NMR spectra were recorded at 25 °C for samples in $CDCl_3$, D_2O, and $(CD_3)_2CO$, while samples in DMSO-d_6 were recorded at temperatures ranging from 25 to 90 °C. Mass spectra of compound **7** and 2,6-diphenyl-4,8-bis((triisopropylsilyl)ethynyl-1,5-dihydrobenzo[1,2-d:4,5-d']diimidazole were obtained using magnetic sector CI mass analyzer, while cruciforms **4a**–**4l** were analyzed using QTof mass analyzer. Melting point measurements were performed in open capillary tubes and the reported values are uncorrected. Column chromatography was carried out on silica gel 60, 32–63 mesh and basic aluminum oxide Act. 1, 50–200µm. Analytical TLC was performed on plastic-backed silica gel IB-F plates and aluminum oxide IB-F plates.

Synthesis of 1,2,4,5-benzenetetramine tetrahydrochloride (5).[9] A 1 L Schlenk flask was flushed with nitrogen and charged with 1,3-diamino-4,6-dinitrobenzene[15] (6.00 g, 30.3 mmol), concentrated HCl (311 mL), and EtOH (155 mL). The reaction flask was attached to the condenser and heated at 50 °C with stirring for 10 min. After 10 min, a solution of anhydrous $SnCl_2$ (52.0 g, 274 mmol) in EtOH (80 mL) was added to the reaction mixture. The beaker containing the $SnCl_2$ solution was washed with an additional portion of EtOH (40 mL) and the washings were added to the reaction flask. The reaction was heated at 86 °C for 2 d, to ensure that the reaction went to completion. The reaction resulted in a white precipitate forming in the flask. After cooling, the solution was filtered and the residue was washed with EtOH to give the product as a light pink solid (8.1 g). The crude product was used without further purification. **5**. IR (neat): 2923 (s, $\tilde{\nu}_{N+–H}$), 2495 (s), 1601 (m, $\tilde{\nu}_{C–C}$), 1556 (s), 1511(s, $\tilde{\nu}_{N+–H}$), 1221 (s, $\tilde{\nu}_{C–N}$), 1127 (m), 1054 (w), 860 (m, $\tilde{\nu}_{C–H}$) cm^{-1}. ^{1}H NMR (D_2O, 400 MHz): δ 6.77 (s) ppm. ^{13}C NMR (D_2O, 100 MHz): δ 125.1, 113.5 ppm.

Synthesis of 2,6-diphenyl-1,5-dihydrobenzo[1,2-*d*:4,5-*d'*]diimidazole (6).[4g] In a 500 mL round bottom flask equipped with a condenser, a mixture of **5** (10.3 g, 36.3 mmol), benzoic acid (17.7 g, 145 mmol), and polyphosphoric acid (PPA, 70 g) was heated up to 140 °C. The reaction temperature was slowly increased to 145 °C and maintained at that temperature for 40 h. After the reaction was finished, the mixture was allowed to cool down, and was then poured into ice water. Stirring was continued while the mixture was made very basic by the addition of NaOH pellets (pH=14). The precipitate was filtered, washed with H_2O, and dried in air overnight. The solid was further dried in a rotary evaporator whose bath was heated for 2 h at 80 °C, finally give crude **6** (11.25 g). Because of its low solubility, this material was used for the next step without further purification.

Synthesis of 4,8-dibromo-2,6-diphenyl-1,5-dihydrobenzo[1,2-*d*:4,5-*d'*]diimidazole (7). A 250 mL round bottom flask was charged with DMF (165 mL) and the solvent was stirred vigorously while the ground powder of compound **6** (10.8 g, 34.7 mmol) was added to it. *N*-Bromosuccinimide (NBS, 12.3 g, 69.3 mmol) was added next, and the reaction mixture was stirred at 20 °C for 1 h. The formed precipitate was filtered under reduced pressure, washed with EtOH, and dried in air to obtain 13 g of a white powder, which was the identified as the target compound **7** (mp >350 ^{o}C) .The overall yield for the synthesis of compound **7** from compound **5** in 2 steps is 80%. **7**. IR (neat): 3160 (w, $\tilde{\nu}_{N–H}$), 1560 (m, $\tilde{\nu}_{C=N}$), 1480 (s), 1460 (s), 1330 (m, $\tilde{\nu}_{C–N}$), 1280 (s), 1230 (s), 867 (s), 772 (m), 725 (s), 685 (s, $\tilde{\nu}_{C–Br}$) cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 13.01 (s, 2H), 8.32 (m, 4H), 7.53 (m, 6H) ppm. ^{13}C NMR

(DMSO-d_6, 100 MHz): δ 153.6, 153.3, 140.4, 139.9, 133.1, 132.6, 130.9, 130.0, 129.3, 127.9, 90.9 ppm. HRMS (CI/[M]$^+$): calcd for $C_{20}H_{12}Br_2N_4^+$: 465.9429, found: 465.9435.

Synthesis of 2,6-diphenyl-4,8-bis((triisopropylsilyl) ethynyl-1,5-dihydrobenzo[1,2-*d*:4,5-*d'*]diimidazole. A 500 mL pear-shaped Schlenk flask was charged with compound **7** (13.0 g, 27.8 mmol), $PdCl_2(PPh_3)_2$ (1.95 g, 2.77 mmol), and CuI (1.06 g, 5.56 mmol). The flask was sealed, then evacuated and backfilled with N_2 three times. In a separate flask, a mixture of $(i\text{-Pr})_2NH$ (200 mL), DMF (100 mL), and tris(isopropyl)silylacetylene (TIPSA, 25 mL, 111 mmol) was degassed for 20 min and then slowly transferred, under positive N_2 pressure, via cannula to the reaction flask. The reaction mixture was stirred and heated at 90 °C for 2 d and then cooled to 20 °C. Afterwards, silica gel (150 mL) was added to the reaction mixture, and the solvent was removed under reduced pressure until a brown powder was formed. This powder was subjected to column chromatography on silica gel, using a mixture of CH_2Cl_2 and hexane as an eluent (starting with a 1:1 volume ratio, and proceeding until 7:3 ratio). The solvent was removed in vacuo to give a yellow crude product which was further purified by recrystallization from EtOH (150 mL), finally giving the desired product as a bright yellow powder (16.4 g, mp 310 ^{o}C). IR (neat): 3460 (s, $\tilde{\nu}_{N–H}$), 2940 (s, $\tilde{\nu}_{C–H}$), 2860 (s), 2140 (m, $\tilde{\nu}_{C\equiv C}$), 1480 (m, $\tilde{\nu}_{Si–C}$), 1450 (s), 1330 (s, $\tilde{\nu}_{Si–C}$), 997 (w), 883 (w), 775 (w), 740 (s), 668 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.43 (s, 2H), 8.08 (d, $^3J_{H–H}$ = 6.9 Hz, 4H), 7.52 (m, 6H), 1.27 (m, 42H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.3, 151.8, 142.7, 141.9, 134.4, 133.7, 130.5, 130.3, 129.6, 129.2, 129.1, 126.7, 102.2, 99.8, 97.1, 19.0, 18.9, 11.7, 11.5, 11.3 ppm. HRMS (CI/[M]$^+$): calcd for $C_{42}H_{54}N_4Si_2^+$: 670.3887, found: 670.3871.

Synthesis of 4,8-diethynyl-2,6-diphenyl-1,5-dihydrobenzo[1,2-*d*:4,5-*d'*]diimidazole (8). In a nitrogen-flushed 100 mL flask, tris(isopropyl)silyl-substituted alkyne produced in the previous step (2.00 g, 2.98 mmol) was dissolved in THF (20 mL), and treated with 1M solution of TBAF in THF (6.56 mL, 6.56 mmol). The resulting solution was stirred at 20 °C for 1 h, and a yellow precipitate was formed. The precipitate was collected by filtration and washed with THF. The residue was mixed with

H_2O (150 mL) and sonicated for 10 min to give fraction A. Meanwhile, the solvent in the filtrate was removed under reduced pressure. The remaining solid was mixed with EtOH (10 mL), followed by H_2O (40 mL), to give fraction B. Subsequently, fraction A was combined with fraction B. The mixture was sonicated for 10 min, filtered, washed with H_2O, and dried in vacuo to yield 1.06 g of crude **8** as a dark yellow powder, which was used in the next step without purification. ^1H NMR (DMSO-d_6, 500 MHz): δ 13.03 (s, 2H), 8.32 (d, J=6.9 Hz, 4H), 7.52 (m, 6H), 4.88 (m, 2H) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): δ 153.5, 153.2, 143.0, 142.7, 134.8, 134.5, 130.6, 130.3, 129.3, 127.8, 95.8, 91.4, 90.6, 90.0, 78.3 ppm.

Synthesis of Cruciform 4a. Phenylacetylene (781 mg, 7.65 mmol) was added to a thick-walled microwave pressure vial that contained a mixture of compound **7** (300 mg, 0.64 mmol), $PdCl_2(PPh_3)_2$ (90 mg, 0.13 mmol), CuI (45 mg, 0.24 mmol), Et_3N (5 mL), and DMF (5 mL). The vial was sealed under nitrogen and exposed to microwave irradiation for 12 h at 110 °C. After cooling, the reaction mixture was extracted with EtOAc, washed with brine, and dried over anhydrous $MgSO_4$. Afterward, Al_2O_3 (80 g) was added to the combined organic layer and the solvent was removed under reduced pressure until a brown powder formed, which was purified by gradient elution column chromatography on alumina (300 g) using EtOAc and hexane as eluents (starting volume ratio 3:17, ending volume ratio 9:11). The solvent was removed in vacuo to yield the crude product which was further purified by recrystallization from THF to give **4a** as a yellow powder (153 mg, 47%, mp 309 °C with decomposition). UV/Vis (THF): λ_{max} (log ε) 386 (4.90) nm. IR (neat): 3056 (w, $\tilde{\nu}_{N-H}$), 2160 (w, $\tilde{\nu}_{C\equiv C}$), 1958 (w), 1596 (m, $\tilde{\nu}_{C=N}$), 1557 (w), 1526 (w), 1476 (s), 1454 (s), 1441 (w), 1402 (m), 1342 (s), 1280 (m), 1215 (w), 1177 (w), 1156 (w), 1115 (w), 1069 (m), 1028 (m), 999 (w), 943 (m), 913 (w), 775 (m), 752 (s), 728 (m), 686 (s), 624 (s), 565 (w) cm^{-1}. ^1H NMR (DMSO-d_6, 600 MHz): δ 12.96 (s, 2H), 8.34 (d, $^3J_{H-H}$ = 7.6 Hz, 4H), 7.78 (m, 4H), 7.56 (t, $^3J_{H-H}$ = 7.6 Hz, 4H), 7.51 (m, 8H) ppm. ^{13}C NMR (DMSO-d_6, 150 MHz, 40 °C): δ 153.5, 142.6, 134.0, 130.5, 129.3, 127.9, 123.7, 103.7, 98.7, 96.6, 89.9, 86.4, 84.6, 82.9 ppm. HRMS (ESI/[M]$^+$): calcd for $C_{36}H_{22}N_4^+$: 510.1844, found: 510.1849.

Synthesis of Cruciform 4b. Anhydrous K_2CO_3 (1.11 g, 8.00 mmol) was added to a solution of 2-(4-(*N*, *N*-dimethylamino)phenyl) trimethylsilylethyne (875 mg, 4.00 mmol) in a mixture of MeOH (5 mL) and THF (5 mL). After stirring for 30 min under nitrogen, the reaction mixture was filtered through Celite. The solvent was removed under reduced pressure to yield crude 4-ethynyl-*N*,*N*-dimethylaniline, which was used without purification in the next step. To minimize manipulations of this compound, we assumed a 95% yield for this reaction.[4g]

The entire amount of 4-ethynyl-*N*,*N*-dimethylaniline (prepared as described above) was added to a thick-walled microwave pressure vial that contained a mixture of compound **7** (300 mg, 0.64 mmol), $PdCl_2$ $(PPh_3)_2$ (90 mg, 0.13 mmol), CuI (45 mg, 0.24 mmol), Et_3N (5 mL), and DMF (5 mL). The vial was sealed under nitrogen and exposed to microwave irradiation for 12 h at 100 °C. After cooling, the reaction mixture was extracted with EtOAc, washed with brine, and dried over anhydrous $MgSO_4$. Afterward, 80 g of aluminum oxide was added to the combined organic layer and the solvent was removed under reduced pressure until a brown powder was formed, which was purified by gradient elution column chromatography on alumina, using EtOAc/hexane eluent system (solvent ratios ranging from 4:16 to 9:11). The solvent was removed in vacuo to give the crude product, which was further purified by recrystallization from THF to afford 214 mg (56%, 0.36 mmol) of a tangelo-colored powder (**4b,** mp 220 ^{o}C, with decomposition). UV/Vis (THF): λ_{max} (log ε) 386 (4.81), 425 (4.70) nm. IR (neat): 3086 (w, $\tilde{\nu}_{N\text{–}H}$), 2190 (s, $\tilde{\nu}_{C\equiv C}$), 1604 (s, $\tilde{\nu}_{C=N}$), 1530 (m), 1514 (m), 1479 (m), 1457 (m), 1402 (w), 1345 (s), 1290 (m), 1232 (m), 1183 (s), 1065 (m), 1029 (m), 999 (w), 945 (m), 920 (w), 843 (w), 810 (s), 777 (m),725 (m), 690 (s), 634 (w), 580 (w) cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.90 (d, $^{3}J_{H\text{–}H}$=5.2 Hz, 2H), 8.34 (m, 4H), 8.57 (m, 10H), 6.79 (d, $^{3}J_{H\text{–}H}$=8.6 Hz, 4H), 2.98 (s, 12H) ppm. ^{13}C NMR (DMSO-d_6, with 20 mg of TBAF trihydrate added, 150 MHz): δ 159.5, 149.3, 146.5, 139.9, 132.1, 127.9, 126.6, 125.3, 114.0, 112.8, 96.1, 94.0, 91.8, 51.9 ppm. HRMS (ESI/[M]$^{+}$): calcd for $C_{40}H_{32}N_6^{+}$ 596.2688, found 596.2692.

Synthesis of Cruciform 4c. A mixture of compound **8** (300 mg, 0.84 mmol), 4-iodotoluene (913 mg, 4.19 mmol), $PdCl_2(PPh_3)_2$ (50 mg, 0.07 mmol) and CuI (27 mg, 0.14 mmol) was added to a 100 mL pear-shaped Schlenk flask. The flask was sealed, and then evacuated and backfilled with nitrogen three times. In a separate flask, a mixture of Et_3N (25 mL) and THF (17 mL) was degassed for 30 min and transferred slowly under positive N_2 pressure via cannula to the reaction flask. The reaction mixture was stirred and heated at 65 °C for 24 h and then cooled to 20 °C. Afterwards, aluminum oxide was added to the reaction mixture and the solvent was removed under reduced pressure until a brown powder was formed, which was subsequently purified by gradient elution column chromatography on alumina, using EtOAc/hexane eluent system (volume ratios ranging from 3:17 to 9:11). The solvent was removed in vacuo to give the crude product, which was further purified by recrystallization from THF to afford cruciform **4c** as a yellow powder (174 mg, 38%, mp 293 °C). UV/Vis (THF): λ_{max} (log ε) 386 (4.91) nm. IR (neat): 3000 (w, $\tilde{\nu}_{N-H}$), 2188 (w, $\tilde{\nu}_{C\equiv C}$), 1603 (m, $\tilde{\nu}_{C=N}$), 1560 (w), 1528 (w), 1505 (m), 1480 (s), 1454 (s), 1401 (m), 1336 (s), 1286 (m), 1254 (m), 1236 (m), 1176 (m), 1109 (w), 1070 (w), 1030 (m), 987 (w), 935 (m), 809 (s), 774 (s), 738 (w), 723 (m), 692 (s), 632 (w) cm^{-1}. ^1H NMR (DMSO-d_6, 500 MHz): δ 12.97 (s, 2H), 8.34 (d, $^3J_{H-H}$ = 7.5 Hz, 4H), 8.57 (m, 10H), 7.32 (d, $^3J_{H-H}$ = 5.7 Hz, 4H), 2.38 (s, 6H) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz, 90 °C): δ 153.3, 138.9, 132.1, 130.7, 130.5, 129.8, 129.2, 128.0, 120.9, 21.6 ppm. HRMS (ESI/$[M]^+$): calcd for $C_{38}H_{26}N_4^+$: 538.2157, found: 538.2138.

Synthesis of Cruciform 4d. A mixture of compound **8** (300 mg, 0.84 mmol), 4-iodoanisole (979 mg, 4.19 mmol), $PdCl_2(PPh_3)_2$ (50 mg, 0.07 mmol), and CuI (27 mg, 0.14 mmol) was added to a 100 mL pear-shaped Schlenk flask. The flask was sealed, then evacuated and backfilled with nitrogen three times. In a separate flask, a mixture of Et_3N (25 mL) and THF (17 mL) was degassed for 30 min and transferred slowly under positive N_2 pressure via cannula to the reaction flask. The reaction mixture was stirred and heated at 65 °C for 24 h and then cooled to 20 °C. Afterwards, 80 g of aluminum oxide was added to the reaction mixture and the solvent was removed under reduced pressure until a brown powder was formed. This powder was purified by gradient elution column chromatography on alumina, using EtOAc/hexane eluent system (volume ratio ranging from 7:13 to 4:1). The solvent was removed in vacuo to give the crude product, which was further purified by recrystallization from THF to afford cruciform **4d** as a yellow powder (196 mg, 41%, mp 280 °C). UV/Vis (THF): λ_{max} (log ε) 385 (4.93) nm. IR (neat): 3062 (w, $\tilde{\nu}_{N-H}$), 2834 (w, $\tilde{\nu}_{C-H}$), 2195 (m, $\tilde{\nu}_{C\equiv C}$), 1603 (s, $\tilde{\nu}_{C=N}$), 1567 (w), 1524 (w), 1504 (s), 1478 (s), 1453 (s), 1399 (m), 1340 (s), 1288 (s), 1244 (s), 1169 (s), 1106 (m), 1071 (w), 1027 (s), 942 (m), 827 (s), 774 (s), 727 (m), 689 (s), 644 (w), 633 (w), 589 (s), 564 (m), 546 (m), 529 (s) cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz at 90 °C): δ 12.69 (s, 2H), 8.33 (d, $^{3}J_{H-H}$ = 6.9 Hz, 4H), 7.71 (s, 4H), 7.52 (m, 6H), 7.05 (d, $^{3}J_{H-H}$ = 8.6 Hz, 4H), 3.84 (s, 6H) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz, 90 °C): δ 160.4, 153.2, 142.0, 133.7, 130.7, 130.4, 129.1, 128.0, 116.0, 115.0, 98.9, 96.9, 83.4, 56.0 ppm. HRMS (ESI/[M]$^+$): calcd for $C_{38}H_{26}N_4O_2^+$: 570.2056, found: 570.2056.

Synthesis of Cruciform 4e. A mixture of compound **8** (300 mg, 0.84 mmol), 4-fluoroiodobenzene (0.56 mL, 4.85 mmol), $PdCl_2(PPh_3)_2$ (50 mg, 0.07 mmol), and CuI (27 mg, 0.14 mmol) was added to a 100 mL pear-shaped Schlenk flask. The flask was sealed, then evacuated and backfilled with nitrogen three times. In a separate flask, a mixture of Et_3N (25 mL) and THF (17 mL) was degassed for 30 min and then transferred slowly under positive N_2 pressure via cannula to the reaction flask. The reaction mixture was stirred and heated at 65 °C for 24 h and then cooled to 20 °C. Afterwards, alumina was added to reaction mixture and the solvent was removed under reduced pressure until a brown powder was formed. This powder was then purified by gradient elution column chromatography on alumina, using EtOAc/hexane eluent system (volume ratio ranging from 1:3 to 1:1). The solvent was removed by vacuum to give the orange crude product which was further purified by recrystallization from EtOAc, to afford cruciform **4e** (187 mg, 41%, mp 287 °C). UV/Vis (THF): λ_{max} (log ε) 383 (4.89) nm. IR (neat): 3066 (w, $\tilde{\nu}_{N-H}$), 2158 (w, $\tilde{\nu}_{C\equiv C}$), 1602 (m, $\tilde{\nu}_{C=N}$), 1558 (w), 1525 (w), 1503 (s), 1477 (s), 1455 (s), 1402 (m), 1342 (s), 1317 (w), 1288 (s), 1235 (s), 1169 (s), 1105 (m), 1064 (w), 1028 (s), 943 (m), 832 (s), 775 (s), 747 (w), 728 (m), 689 (s), 634 (w), 582 (s), 566 (w), 556 (w), 547 (w), 530 (s) cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 13.05 (d, $^{3}J_{H-H}$ = 8.0 Hz, 2H), 8.33 (m, 4H), 7.84 (m, 4H), 7.55 (m, 6H), 7.36 (m, 4H) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): δ 163.7, 161.6, 153.4, 142.3, 134.5, 130.7, 129.3, 127.7, 120.0, 116.6, 97.6, 96.4, 84.3 ppm. HRMS (ESI/[M]$^+$): calcd for $C_{36}H_{20}F_2N_4^+$: 546.1656, found: 546.1656.

Synthesis of Cruciform 4f. A mixture of compound **8** (300 mg, 0.84 mmol), 1-iodo-4-nitrobenzene (834 mg, 3.35 mmol), $PdCl_2(PPh_3)_2$ (50 mg, 0.07 mmol), and CuI (27 mg, 0.14 mmol) was placed in a 100 mL pear-shaped Schlenk flask. The flask was sealed, then evacuated and backfilled with nitrogen three times. In a separate flask, a mixture of Et_3N (30 mL) and THF (20 mL) was degassed for 30 min and then transferred slowly under positive nitrogen pressure via cannula into the reaction flask. The reaction mixture was stirred and heated at 50 °C for 24 h, then cooled to 20 °C, filtered, and washed with THF (5 mL). The residue collected was recrystallized from THF to give the crude product, which was then mixed with H_2O (150 mL), sonicated for 30 min, filtered, and dried in air to give cruciform **4f** (136 mg, 27%) as a red powder (mp 327 °C, with decomposition). UV/Vis (THF): λ_{max} (log ε) 388 (4.80) nm. IR (neat): 3060 (w, $\tilde{\nu}_{N-H}$), 2199 (w, $\tilde{\nu}_{C\equiv C}$), 1591 (m, $\tilde{\nu}_{C=N}$), 1514 (s, $\tilde{\nu}_{NO2}$), 1476 (m), 1454 (m), 1402 (w), 1337 (s, $\tilde{\nu}_{NO2}$), 1175 (w), 1106 (m), 1028 (w), 994 (w), 943 (w), 854 (s), 775 (m), 748 (m), 728 (w), 687 (s), 568 (w) cm^{-1}. ^1H NMR (DMSO-d_6, 500 MHz): δ 13.29 (s, 2H), 8.34 (apparent d, $^3J_{H-H}$ = 6.9 Hz, 8H), 8.01 (br s, 4H), 7.57 (m, 6H) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): δ 133.2, 131.1, 130.0, 129.5, 128.1, 124.4 ppm (because of the low solubility of cruciform **4f**, a satisfactory ^{13}C NMR spectrum could not be obtained; listed are all the observed peaks). HRMS (ESI/$[M]^+$): calcd for $C_{36}H_{20}N_6O_4^+$: 600.1546, found: 600.1526.

Synthesis of Cruciform 4g. A mixture of compound **8** (300 mg, 0.84 mmol), 4-iodobenzotrifluoride (0.50 mL, 3.40 mmol), $PdCl_2(PPh_3)_2$ (50 mg, 0.07 mmol), and CuI (27 mg, 0.14 mmol) was placed in a 100 mL pear-shaped Schlenk flask. The flask was sealed, then evacuated and backfilled with nitrogen three times. A mixture of Et_3N (30 mL) and THF (20 mL) was degassed for 30 min and transferred slowly under positive nitrogen pressure via cannula into the reaction flask. The reaction mixture was stirred and heated at 65 °C for 24 h, then cooled to 20 °C. Afterwards, silica gel was added to the reaction mixture, and the solvent was removed under reduced pressure until a brown powder was formed. This powder was purified by gradient elution column chromatography on silica gel, using EtOAc/hexane eluent system (volume ratio ranging from 1:3 to 1:1). The solvent was removed in vacuo to give the yellow crude product, which was further purified by recrystallization from Et_2O, to yield cruciform **4g** (220 mg, 41%) as a yellow powder (mp 245 °C, with decomposition). UV/Vis (THF): λ_{max} (log ε) 392 (4.86) nm. IR (neat): 3062 (w, $\tilde{\nu}_{N-H}$), 2201 (w, $\tilde{\nu}_{C\equiv C}$), 1613 (m, $\tilde{\nu}_{C=N}$), 1563 (w), 1529 (w), 1505 (w), 1478 (s), 1455 (s), 1403 (m), 1341 (s), 1317 (s), 1290 (s), 1246 (m), 1167 (s), 1119 (s), 1103 (s), 1064 (s), 1028 (s), 1018 (s), 945 (m), 837 (s), 774 (s), 747 (w, $\tilde{\nu}_{CF3}$), 728 (m), 689 (s), 634 (w), 592 (s), 537 (m) cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 13.16 (s, 2H), 8.34 (d, $^{3}J_{H-H}$ = 7.5 Hz, 4H), 8.00 (m, 8H), 7.55 (m, 6H) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): δ 153.5, 142.6, 134.2, 132.9, 130.9, 130.2, 129.4, 127.9, 126.2, 125.7, 123.5, 97.4, 96.3, 87.1 ppm. HRMS (ESI/[M]$^+$): calcd for $C_{38}H_{20}F_6N_4^+$: 646.1592, found: 646.1592.

Synthesis of Cruciform 4h. A mixture of compound **8** (300 mg, 0.84 mmol), 2-iodothiophene (0.55 mL, 4.98 mmol), $PdCl_2(PPh_3)_2$ (50 mg, 0.07 mmol), and CuI (27 mg, 0.14 mmol) was placed in a 100 mL pear-shaped Schlenk flask. The flask was sealed, then evacuated and backfilled with nitrogen three times. A solution of Et_3N (25 mL) and THF (17 mL) was degassed for 30 min and then transferred slowly under positive nitrogen pressure via cannula into the reaction flask. The reaction mixture was stirred and heated at 65 °C for 24 h and then cooled to 20 °C. Afterwards, alumina was added to the reaction mixture and the solvent was removed under reduced pressure until a brown powder was formed. This powder was purified by gradient elution column chromatography on alumina, using EtOAc/hexane eluent system (volume ratio ranging from 1:4 to 3:2). The solvent was removed in vacuo to give the crude product which was further purified by recrystallization from THF/hexane to yield cruciform **4h** (153 mg, 35%) as a dark yellow powder (mp 268 °C, with decomposition). **4h**: UV/Vis (THF): λ_{max} (log ε) 391 (4.89) nm. IR (neat): 3111 (w, $\tilde{\nu}_{C-H\text{-thiophene}}$), 3060 (w, $\tilde{\nu}_{N-H}$), 2190 (w, $\tilde{\nu}_{C\equiv C}$), 1613 (w, $\tilde{\nu}_{C=N}$), 1562 (w), 1531 (w), 1506 (w), 1479 (m), 1454 (s), 1396 (w), 1341 (s), 1325 (s), 1276 (m), 1226 (s), 1174 (w), 1071 (w), 1043 (s), 1029 (m), 965 (w), 942 (m), 918 (w), 851 (s), 831 (m), 774 (s), 744 (w), 686 (s), 625 (m) cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 13.12 (s, 2H), 8.32 (d, $^{3}J_{H-H}$ = 7.5 Hz, 4H), 8.56 (m, 10H), 7.20 (m, 2H) ppm. ^{13}C NMR (Me_2CO-d_6 and 200 mg of TBAF trihydrate, 150 MHz): δ 131.2, 128.0, 127.2, 127.1, 126.2, 125.8, 88.7 ppm. HRMS (ESI/[M]$^+$): calcd for $C_{32}H_{18}N_4S_2^+$: 522.0973, found: 522.0959.

Synthesis of Cruciform 4i. A mixture of compound **8** (300 mg, 0.84 mmol), 4-iodoacetophenone (618 mg, 2.51 mmol), $PdCl_2(PPh_3)_2$ (50 mg, 0.07 mmol), and CuI (27 mg, 0.14 mmol) was placed in a 100 mL pear-shaped Schlenk flask. The flask was sealed, then evacuated and backfilled with nitrogen three times. In a separate flask, a mixture of Et_3N (30 mL) and THF (20 mL) was degassed for 30 min and transferred slowly under positive nitrogen pressure via cannula into the reaction flask. The reaction mixture was stirred and heated at 65 °C for 2 d, then cooled to 20 °C, filtered, and washed with THF (5 mL). The residue collected was recrystallized from THF to give the crude product, which was mixed with H_2O (150 mL), sonicated for 30 min, filtered, and dried in air to give cruciform **4i** (300 mg, 60%) as a yellow powder (mp 352 ^{o}C, with decomposition). UV/Vis (THF): λ_{max} (log ε) 382 (4.60) nm. IR (neat): 3199 (w, $\tilde{\nu}_{N-H}$), 2204 (w, $\tilde{\nu}_{C\equiv C}$), 1668 (s), 1602 (s, $\tilde{\nu}_{C=N}$), 1557 (w), 1505 (w), 1480 (m), 1455 (s), 1402 (m), 1336 (s), 1312 (w), 1273 (s), 1168 (m), 1105 (m), 1064 (m), 1029 (m), 1017 (w), 940 (w), 829 (s), 777 (s), 747 (w), 728 (m), 689 (s), 593 (m) cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz, 40 °C): δ 13.10 (s, 2H), 8.35 (d, $^{3}J_{H-H}$ = 6.9 Hz, 4H), 8.06 (d, $^{3}J_{H-H}$ = 7.5 Hz, 4H), 7.90 (s, 4H), 7.55 (m, 6H), 2.62 (s, 6H) ppm.^{13}C NMR (DMSO-d_6, 125 MHz, 40 °C): δ 197.8, 154.1, 136.8, 132.3, 130.8, 130.3, 129.3, 129.0, 128.0, 98.3, 27.3 ppm (because of the low solubility of cruciform **4i**, a satisfactory ^{13}C NMR spectrum could not be obtained; listed are all the observed peaks). HRMS (ESI/[M]$^+$): calcd for $C_{40}H_{26}N_4O_2^+$: 594.2056, found: 594.2050.

Synthesis of Cruciform 4j. A mixture of compound **8** (300 mg, 0.84 mmol), ethyl 4-iodobenzoate (0.56 mL, 3.33 mmol), $PdCl_2(PPh_3)_2$ (50 mg, 0.07 mmol), and CuI (27 mg, 0.14 mmol) was added to a 100 mL pear-shaped Schlenk flask. The flask was sealed, then evacuated and backfilled with nitrogen three times. In a separate flask, a solution of Et_3N (30 mL) and THF (20 mL) was degassed for 30 min and then transferred slowly under positive nitrogen pressure via cannula into the reaction flask. The reaction mixture was stirred and heated at 65 °C for 24 h and then cooled to 20 °C, filtered and washed with THF (5 mL). The residue collected was recrystallized from a THF/EtOAc mixture (volume ratio 2:3), to give the crude product which was then mixed with H_2O (150 mL), sonicated for 30 min, filtered and dried in air, to finally give cruciform **4j** (310 mg, 57%) as a yellow powder (mp 268 °C, with decomposition). UV/Vis (THF): λ_{max} (log ε) 394 (4.89) nm. IR (neat): 3253 (m), 2981 (w, $\tilde{\nu}_{N-H}$), 2205 (w, $\tilde{\nu}_{C\equiv C}$), 1694 (s, $\tilde{\nu}_{C=O}$), 1605 (m, $\tilde{\nu}_{C=N}$), 1561 (w), 1524 (w), 1504 (m), 1480 (s), 1454 (s), 1404 (m), 1365 (w), 1339 (s), 1308 (w), 1287 (s, $\tilde{\nu}_{CO-O}$), 1275 (s), 1172 (m), 1128 (m), 1106 (s), 1071 (w), 1021 (m), 987 (w), 941 (m), 853 (m), 830 (w), 773 (s), 765 (m), 725 (m), 687 (s), 652 (w) cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 13.15 (d, $^3J_{H-H}$ = 5.0 Hz, 2H), 8.35 (m, 4H), 8.00 (m, 8H), 7.55 (m, 6H), 4.33 (q, $^3J_{H-H}$ = 7.3 Hz, 4H), 1.33 (t, $^3J_{H-H}$ = 7.3 Hz, 6H) ppm.^{13}C NMR (DMSO-d_6, 100 MHz): δ 165.8, 153.6, 142.7, 134.1, 132.4, 130.9, 130.2, 129.9, 129.4, 128.0, 98.1, 96.3, 87.6, 61.6, 14.7 ppm. HRMS (ESI/$[M]^+$): calcd for $C_{42}H_{30}N_4O_4^+$: 654.2267, found: 654.2270.

Synthesis of Cruciform 4l. A mixture of compound **8** (500 mg, 1.39 mmol), 4-(iodophenyl)tetrahydropyran-2-yl ether[16] (1.73 g, 5.58 mmol), $PdCl_2(PPh_3)_2$ (83 mg, 0.12 mmol), and CuI (45 mg, 0.24 mmol) was added to a 100 mL pear-shaped Schlenk flask. The flask was sealed, then evacuated and backfilled with nitrogen three times. In a separate flask, a solution of Et_3N (40 mL) and THF (27 mL) was degassed for 30 min and then transferred slowly under positive N_2 pressure via cannula into the reaction flask. The reaction mixture was stirred and heated at 60 °C for 36 h, then cooled to 20 °C. Afterwards, alumina was added to the reaction mixture, and the solvent was removed under reduced pressure until a brown powder was formed. This powder was purified by gradient elution column chromatography on alumina, using EtOAc/hexane eluent system (volume ratio ranging from 25:75 to 55:45). The solvent was removed in vacuo to give 590 mg of the crude cruciform **4k** as the intermediate.

In a 250 mL round-bottom flask, trifluoroacetic acid (4.5 mL) was added to a solution of the aforementioned cruciform **4k** (590 mg, 0.83 mmol) in DCM (150 mL), which was kept in a dry ice/Me_2CO bath. The reaction was stirred for 2 h at –78 °C and then warmed up to 20 °C.[17] The precipitate formed in the reaction was collected by filtration and washed with DCM. Afterwards, it was mixed with water (500 mL), sonicated for 30 min, filtered, and dried in air to give the crude product, which was further purified by recrystallization from THF to afford cruciform **4l** (310 mg, 41%) as a yellow powder (mp 320 °C, with decomposition). UV/Vis (THF): λ_{max} (log ε) 383 (4.95) nm. IR (neat):

3410 (w, $\tilde{\nu}_{O-H}$), 3063 (w, $\tilde{\nu}_{N-H}$), 2204 (w, $\tilde{\nu}_{C\equiv C}$), 1604 (s, $\tilde{\nu}_{C=N}$), 1525 (w), 1505 (s), 1479 (s), 1454 (s), 1402 (w), 1380 (w), 1345 (m), 1278 (m), 1265 (w), 1243 (s), 1169 (s), 1105 (w), 1072 (w), 1028 (m), 946 (w), 828 (s), 776 (s), 727 (w), 692 (s), 684 (s), 634 (w), 616 (w), 591 (s), 567 (w), 534 (s) cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.95 (s, 2H), 9.97 (s, 2H), 8.33 (d, $^{3}J_{H-H}$ = 7.5 Hz, 4H), 8.52 (m, 10H), 6.87 (d, $^{3}J_{H-H}$ = 8.0 Hz, 4H) ppm.^{13}C NMR (DMSO-d_6, 125 MHz): δ 158.7, 153.1, 142.4, 133.9, 130.6, 129.3, 127.8, 116.3, 113.9, 99.4, 96.6, 82.5 ppm. HRMS (ESI/[M]$^+$): calcd for $C_{36}H_{22}N_4O_2^{+}$: 542.1743, found: 542.1742.

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Supporting Information. Additional experimental and computational details, and spectroscopic characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES

(1) For selected example of different cruciform motifs, see: (a) Bhaskar, A.; Guda, R.; Haley, M. M.; Goodson, T. III *J. Am. Chem. Soc.* **2006**, *128*, 13972–13973. (b) Marsden, J. A.; Miller, J. J.; Shirtcliff, L. D.; Haley, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 2464–2476. (c) Davey, E. A.; Zucchero, A. J.; Trapp, O.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2011**, *133*, 7716–7718. (d) McGrier, P. L.; Solntsev, K. M.; Zucchero, A. J.; Miranda, O. R.; Rotello, V. M.; Tolbert, L. M.; Bunz, U. H. F. *Chem. Eur. J.* **2011**,

17, 3112–3119. (e) Zucchero, A. J.; McGrier, P. L.; Bunz, U. H. F. *Acc. Chem. Res.* **2010**, *43*, 397–408. (f) Tolosa, J.; Zucchero, A. J.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2008**, *130*, 6498–6506. (g) Zucchero, A. J.; Wilson, J. N.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2006**, *128*, 11872–11881. (h) Kang, H.; Evmenenko, G.; Dutta, P.; Clays, K.; Song, K.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 6194–6205. (i) Kang, H.; Zhu, P.; Yang, Y.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 15974–15975. (j) Gisselbrecht, J. P.; Moonen, N. N. P.; Boudon, C.; Nielsen, M. B.; Diederich F.; Gross, M. *Eur. J. Org. Chem.* **2004**, 2959–2972. (k) Mitzel, F.; Boudon, C.; Gisselbrecht, J. P.; Seiler, P.; Gross, M.; Diederich, F. *Helv. Chim. Acta* **2004**, *87*, 1130–1157. (l) Hilger, A.; Gisselbrecht, J.-P.; Tykwinski, R. R.; Boudon, C.; Schreiber, M.; Martin, R. E.; Lüthi, H. P.; Gross, M.; Diederich, F. *J. Am. Chem. Soc.* **1997**, *119*, 2069–2078. (m) Koenen, J.-M.; Bilge, A.; Allard, S.; Alle, R.; Meerholz, K.; Scherf, U. *Org. Lett.* **2009**, *11*, 2149–2152. (n) Zen, A.; Bilge, A.; Galbrecht, F.; Alle, R.; Meerholz, K.; Grenzer, J.; Neher, D.; Scherf, U.; Farrell, T. *J. Am. Chem. Soc.* **2006**, *128*, 3914–3915.

(2) (a) Feldman, A. K.; Steigerwald, M. L.; Guo, X.; Nuckolls, C. *Acc. Chem. Res.* **2008**, *41*, 1731–1741. (b) Tang, J.; Wang, Y.; Klare, J. E.; Tulevski, G. S.; Wind, S. J.; Nuckolls, C. *Angew. Chem. Int. Ed.* **2007**, *46*, 3892–3895. (c) Florio, G. M.; Klare, J. E.; Pasamba, M. O.; Werblowsky, T. L.; Hyers, M.; Berne, B. J.; Hybertsen, M. S.; Nuckolls, C.; Flynn, G. W. *Langmuir* **2006**, *22*, 10003–10008. (d) Guo, X.; Small, J. P.; Klare, J. E.; Wang, Y.; Purewal, M. S.; Tam, I. W.; Hong, B. H.; Caldwell, R.; Huang, L.; O'Brien, S.; Yan, J.; Breslow, R.; Wind, S. J.; Hone, J.; Kim, P.; Nuckolls, C. *Science* **2006**, *311*, 356–359. (e) de Picciotto, A.; Klare, J. E.; Nuckolls, C.; Baldwin, K.; Erbe, A.; Willett, R. *Nanotechnology* **2005**, *16*, 3110–3114. (f) Klare, J. E.; Tulevski, G. S.; Nuckolls, C. *Langmuir* **2004**, *20*, 10068–10072. (g) Klare, J. E.; Tulevski, G. S.; Sugo, K.; de Picciotto, A.; White, K. A.; Nuckolls, C. *J. Am. Chem. Soc.* **2003**, *125*, 6030–6031.

(3) (a) Tlach, B.C.; Tomlinson, A.L.; Morgan, K.D.; Collins, C.R.; Jeffries-EL, M. *Aust. J. Chem.* **2014**, *67*, 711–721. (b) Tlach, B. C.; Tomlinson, A. L.; Ryno, A. G.; Knoble, D. D.; Drochner, D. L.;

Krager, K. J.; Jeffries-EL, M. *J. Org. Chem.* **2013**, *78*, 6570–6581. (c) Intemann, J. J.; Hellerich, E. S.; Tlach, B. C.; Ewan, M. D.; Barnes, C. A.; Bhuwalka, A.; Cai, M.; Shinar, J.; Shinar, R.; Jeffries-EL, M. *Macromolecules* **2012**, *45*, 6888–6897. (d) Klimavicz, J. S.; Mike, J. F.; Bhuwalka, A; Tomlinson, A. L.; Jeffries-EL, M *Pure Appl. Chem*. **2012**, *84*, 991–1004. (e) Tlach, B. C.; Tomlinson, A. L.; Bhuwalka, A.; Jeffries-EL, M. *J. Org. Chem.* **2011**, *76*, 8670–8681. (f) Mike, J. F.; Makowski, A. J.; Jeffries-EL, M. *Org. Lett.* **2008**, *10*, 4915–4918.

(4) (a) Saeed, M. A.; Le, H. T. M.; Miljanić, O. Š. *Acc. Chem. Res.* **2014**, *47*, 2074–2083. (b) Martínez-Martínez, V.; Lim, J.; Bañuelos, J.; López-Arbeloa, I.; Miljanić, O. Š. *Phys. Chem. Chem. Phys.* **2013**, *15*, 18023–18029. (c) Jo, M.; Lim, J.; Miljanić, O. Š. *Org. Lett.* **2013**, *15*, 3518–3521. (d) Lim, J.; Miljanić, O. Š. *Chem. Commun.* **2012**, *48*, 10301–10303. (e) Lim, J.; Osowska, K.; Armitage, J. A.; Martin, B. R.; Miljanić, O. Š. *CrystEngComm* **2012**, *14*, 6152–6162. (f) Lim, J.; Nam, D.; Miljanić, O. Š. *Chem. Sci.* **2012**, *3*, 559–563. (g) Lim, J.; Albright, T. A.; Martin, B. R.; Miljanić, O. Š. *J. Org. Chem.* **2011**, *76*, 10207–10219. (h) Osowska, K.; Miljanić, O. Š. *Chem. Commun.* **2010**, *46*, 4276–4278.

(5) Lirag, R. C.; Le, H. T. M.; Miljanić, O. Š. *Chem. Commun.* **2013**, *49*, 4304–4306.

(6) (a) Boydston, A. J.; Pecinovsky, C. S.; Chao, S. T.; Bielawski, C. W. *J. Am. Chem. Soc.* **2007**, *129*, 14550–14551. (b) Boydston, A. J.; Vu, P. D.; Dykhno, O. L.; Chang, V.; Wyatt, A. R. II; Stockett, A. S.; Ritschdorff, E. T.; Shear, J. B.; Bielawski, C. W. *J. Am. Chem. Soc.* **2008**, *130*, 3143–3156. (c) Boydston, A. J.; Khramov, D. M.; Bielawski, C. W. *Tetrahedron Lett.* **2006**, *47*, 5123–5125. (d) Khramov, D. M.; Boydston, A. J.; Bielawski, C. W. *Org. Lett.* **2006**, *8*, 1831–1834.

(7) Hegedus, L. S.; Odle, R. R.; Winton, P. M.; Weider, P. R. *J. Org. Chem*. **1982**, *47*, 2607–2613.

(8) (a) Zhang, L.-P.; Jiang, K.-J.; Li, G.; Zhang, Q.-Q.; Yang, L.-M. *J. Mater. Chem. A* **2014**, *2*, 14852–14857. (b) Li, H.; Kim, F. S.; Ren, G.; Hollenbeck, E. C.; Subramaniyan, S.; Jenekhe, S. A. *Angew. Chem. Int. Ed.* **2013**, *52*, 5513–5517.

(9) Nihei, M.; Kurihara, M.; Mizutani, J.; Nishihara, H. *J. Am. Chem. Soc.* **2003**, *125*, 2964–2973.

(10) Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

(11) For example, cruciform **4j** appears to have fluorescence quantum yield of 98% (measured using 9,10-diphenylanthracene as the standard). We will elaborate on this finding and other related studies in a future paper dealing exclusively with the photophysics of benzobisimidazole cruciforms.

(12) Walba, H.; Isensee, R. W. *J. Org. Chem.* **1961**, *26*, 2789–2791.

(13) (a) Phan, A.; Doonan, C. J.; Uribe-Romo, F. J.; Knobler, C. B.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2010**, *43*, 58–67. (b) Park, K. S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R. D.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 10186–10191.

(14) Takayama, Y.; Yamada, T.; Tatekabe, S.; Nagasawa. K. *Chem. Commun.* **2013**, *49*, 6519–6521.

(15) Boyer, J. H.; Buriks, R. S.; Toggweiler, U. *J. Org. Chem.* **1960**, *82*, 2213–2215.

(16) Li, Y.; Urbas, A.; Li, Q. *J. Org. Chem.* **2011**, *76*, 7148–7156.

(17) McGrier, P. L.; Solntsev, K. M.; Schönhaber, J.; Brombosz, S. M.; Tolbert, L. M.; Bunz, U. H. F. *Chem. Commun.* **2007**, 2127–2129.